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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C07D 213/00, 231/00, 233/00, C07B 61/00

A2

(11) International Publication Number: WO 00/32572

(43) International Publication Date: 8 June 2000 (08.06.00)

(21) International Application Number: PCT/US99/28761

(22) International Filing Date: 3 December 1999 (03.12.99)

(30) Priority Data:
09/205,811 4 December 1998 (04.12.98) US

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(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: COMBINATORIAL DISCOVERY AND TESTING OF IONIC LIQUIDS

(57) Abstract

Arrays of ionic liquids are provided for combinatorial materials science research. These ionic liquids may be characterized by the general formula A^+B^- where A^+ represents any stable inorganic or organic cation and B^- represents any stable organic or inorganic anion. The uses for such arrays are as co-solvents in various chemical reactions.

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COMBINATORIAL DISCOVERY AND TESTING OF IONIC LIQUIDS

This application is a continuation-in-part of pending U.S. patent application 09/205,811 filed December 4, 1998, which is incorporated herein by reference for all purposes.

FIELD OF THE INVENTION

The present invention relates to combinatorial materials science, specifically to libraries of ionic liquids and methods useful for the combinatorial research into the use and discovery of ionic liquids for a variety of reactions, including reactions where the ionic liquid acts as a part of the reaction medium for the reaction. Combinatorial techniques are employed to test the compositions and methods of this invention.

BACKGROUND OF THE INVENTION

Combinatorial materials science generally refers to methods for creating a collection of diverse compounds or materials using a relatively small set of precursors and/or methods for rapidly testing or screening the collection of compounds or materials for desirable performance characteristics and properties. As currently practiced, combinatorial materials science permits scientists to systematically explore the influence of structural variations in candidates by dramatically accelerating the rates at which they are created and evaluated. Compared to traditional discovery methods, combinatorial methods sharply reduce the costs associated with preparing and screening each candidate.

Combinatorial chemistry has revolutionized the process of drug discovery. See, for example, 29 Acc. Chem. Res. 1-170 (1996); 97 Chem. Rev. 349-509 (1997);

S. Borman, Chem. Eng. News 43-62 (Feb. 24, 1997); A. M. Thayer, Chem. Eng. News 57-64 (Feb. 12, 1996); N. Terret, 1 Drug Discovery Today 402 (1996)).

One can view drug discovery as a two-step process: acquiring candidate compounds through laboratory synthesis or through natural product collection, followed by evaluation or screening for efficacy. Pharmaceutical researchers have long used high-throughput screening (HTS) protocols to rapidly evaluate the therapeutic value of natural products and libraries of compounds synthesized and cataloged over many years. However, compared to HTS protocols, chemical synthesis has historically been a slow, arduous process. With the advent of combinatorial methods, scientists can now create large libraries of organic molecules at a pace on par with HTS protocols.

Recently, combinatorial approaches have been used for discovery programs unrelated to drugs. For example, some researchers have recognized that combinatorial strategies also offer promise for the discovery of inorganic compounds such as high-temperature superconductors, magnetoresistive materials, luminescent materials, and catalytic materials. See, for example, co-pending U.S. patent application no. 08/327,513 "The Combinatorial Synthesis of Novel Materials" (published as WO 96/11878), U.S. Patent No. 5,775,359 and co-pending U.S. patent application no. 08/898,715 "Combinatorial Synthesis and Analysis of Organometallic Compounds and Catalysts" (a version of which was published as WO 98/03251), each of which is herein incorporated by reference.

Ionic liquids are known. Ionic liquids are ionic compositions that are molten at low temperature, which are sometimes referred to as molten salts. See Seddon, "Ionic Liquids for Clean Technology", J. Chem. Tech. Biotechnol., 68, pp. 351-356 (1997), incorporated herein by reference. Ionic liquids are known to form part of the reaction media for certain types of reactions. For example, Olivier and Chauvin, "Nonaqueous Room-Temperature Ionic Liquids: A New Class of Solvents for Catalytic Organic Reactions", Chem. Ind. (Dekker) (1996), 68, pp. 249-263, incorporated herein by reference, disclose the use of ionic liquids for dimerization, alkylation, hydrogenation, metathesis, hydroformylation and other reactions. U.S. Patent No. 5,731,101, incorporated herein by reference, discloses use of ionic liquids for alkylation, arylation and polymerization reactions. U.S. Patent No. 5,304,615, incorporated herein by reference, discloses use of ionic liquids as the catalyst for polymerization of an olefinic feedstock, which typically contains a mixture of monomers. See also WO 95/21872, WO 98/03454 and WO 95/21806, each of which is incorporated herein by reference. Similarly ionic compounds are known, see for

example Kawabata et al. Journal of Antibiotics, vol. 48, no. 9, pp. 1049-1051 (1995). Ionic liquids are commercially available, for example from Solvent Innovation GmbH, Cologne, Germany.

Cationic polymerizations are also well known and are described in numerous publications. See, for example G. Odian, Principles of Polymerization (Wiley & Sons, 1991). Cationic polymerization of isoolefins, in particular isobutylene is also well documented. See, for example R. Faust, T. D. Shaffer, Cationic Polymerization (American Chemical Society, 1997). However, there are several disadvantages associated with the known processes, including the use of extremely low temperatures and the need to use polar, volatile solvents such as methyl chloride. There is clearly a need to develop new solvent systems and catalysts, which may be used at higher temperatures.

Despite all of the above, there remains a need to identify the ionic liquids that are commercially useful in particular reactions. For example, none of the cited references has shown the ability to polymerize isobutylenes into a very high molecular weight polymer using an ionic liquid, meaning polyisobutylenes having a weight average molecular weight (Mw) of over 100,000 using an ionic liquid. The difference between very low Mw polyisobutylenes (below about 3,000 Mw), low Mw polyisobutylenes (about 3,000-10,000 Mw), high Mw polyisobutylenes (between about 10,000-100,000 Mw) and very high Mw polyisobutylenes (above 100,000 Mw) is in the properties that such polymers may possess. Very low Mw polyisobutylenes are typically useful in adhesives, lubricants, motor oil and transmission fluids. Low Mw polyisobutylenes are useful in sealants and caulking applications. High Mw polyisobutylenes are useful in rubber products or as impact modifiers of thermoplastics. Very high Mw polyisobutylenes possess unique physical and chemical properties, such as low oxygen permeability and mechanical resilience, finding uses in the automobile industry as rubber products.

Also, the syntheses of very high molecular weight polyisobutylenes are not straightforward. For example, it is well known that to obtain very high Mw polyisobutylenes, extremely low temperatures must be employed in the polymerization reaction. Such temperatures are in the region of about −100 °C. See G. Odian, Principles of Polymerization (Wiley & Sons, 1991), pp. 396-398, incorporated herein by reference. Thus, the molecular weight of polyisobutylenes

produced typically increases as the temperature of the polymerization process decreases. However, U.S. Patent 5,304,615 states that when using ionic liquids as the polymerization medium for isobutylene, either alone or with comonomers, "contrary to expectations, the molecular weight of the product does not increase with decreasing temperatures" (col. 4, lines 5-7). Finally, although U.S. Patent 5,304,615 states that polymers of Mw up to 100,000 can be formed (see Example 2), no one has demonstrated, until this invention, the ability to prepare very high Mw polyisobutylenes with an ionic liquid.

In addition, the discovery of which ionic liquids are most useful for which reactions is a particularly slow process.

SUMMARY OF THE INVENTION

Therefore it is an object of this invention to apply combinatorial techniques to the discovery of ionic liquids for particular reactions. The "combinatorialization" of ionic liquids can be performed by suitable combination of a group of cations with a wide selection of anions. The influence of the resulting solvent system that the employs the ionic liquid is systematically or randomly explored and the optimum solvent or solvent mixture for the particular reaction of interest is identified. It is a further object to improve the efficiency of the research of ionic liquids to the discovery of new compositions for the preparation of polyisoolefins, and in particular very high molecular weight polyisobutylenes, improves the efficiency of discovery efforts. Further objects of this invention will be evident to those of skill in the art upon review of this specification.

In one aspect, this invention provides arrays of ionic liquids where each member of the array may be characterized by the general formula A^+B^- where A^+ represents any stable organic or inorganic cation and B^- represents any stable organic or inorganic anion. Each member of the array differs from other members of the array by having a different chemical composition. The array can be formed in plates that contain a plurality of vials, with each vial holding a member of the array of the ionic liquids, such that each member of the array cannot contact another member of the array.

In another aspect, this invention relates to a method of testing ionic liquids in particular reactions, comprising providing an array of ionic liquids and running the reaction of interest in parallel using the ionic liquids in the array as a component in the reaction, such as the solvent, catalyst, etc. Different ionic liquid compositions can be tested in the reaction of interest. Alternatively, each member of the array can contain the same ionic liquid allowing for process conditions of the reaction to be varied within the array. The reaction of interest can vary widely from combinatorial array to array, with the reactions of interest including cross-coupling, Friedel-Crafts, dimerization, oligomerization, polymerization, hydrogenation, oxidation, dehydrogenation, aromatization, carbonylation, dehydrodimerization, hydrodehalogenation, hydrodesulfurization, oxychlorization, C-C coupling, Heck reaction, amination, amoxidation, alkylation, vinylation, acetoxylations, oxidative esterification, telomerization, hydroxylations of C=C bonds and aromatics, CH hydroxylation, oxidative cleavage, epoxidation, reduction, hydrosilylation and hydroformylation.

In yet another aspect, this invention relates to the combinatorial testing of ionic liquids for the polymerization of olefins or isoolefins or for the copolymerization of an olefin or isoolefin plus additional comonomer. In this aspect, an array of ionic liquids is provided with an aliquot of each member of the array being dispensed into a reactor block containing a plurality of reaction vessels. The other components of the polymerization reaction are added to the reactor vessels (e.g., monomer, catalyst, co-solvents, etc.) and the reaction is carried out in parallel at desired reaction conditions, which may be varied between two or more arrays or within a single array. The order of addition of reaction components depends on the reaction being studied. In alternative embodiments, other compounds may be added to the ionic liquid to form a new catalyst composition, which polymerizes an isoolefin or copolymerizes the isoolefin plus additional comonomer.

In yet another aspect, this invention uses ionic liquids as a portion of the reaction medium for polymerizing of isoolefins into polyisoolefins in a combinatorial manner. In this aspect, the ionic liquid is part of a two or more phase solvent system, with the other portions of the solvent system comprising non-ionic liquids, such as alkanes (e.g., hexane, heptane), cycloalkanes (e.g., cyclohexane, methyl(cyclohexane), aromatics), Isopar E®, etc. Preferably in this embodiment, the

entire system is agitated to increase surface area between phases and where the system includes all solvents, catalysts, monomers, scavengers, etc. The miscibility of the two or more solvents can be adjusted by changing the components of the ionic liquid, such as by varying the chain length of a hydrocarbon portion of the cation or anion in the ionic liquid.

Other aspects of this invention include methods of making arrays of ionic liquids using liquids handling robots or other methods and methods of running reactions in parallel with ionic liquids.

DETAILED DESCRIPTION OF THE INVENTION

The phrases "characterized by the formula" or "represented by the formula" are used in the same way that "comprising" is commonly used. The term "independently selected" is used herein to indicate that the R groups, e.g., R^1, R^2, and R^3, can be identical or different (e.g. R^1, R^2 and R^3 may all be substituted alkyls or R^1 and R^2 may be a substituted alkyl and R^3 may be an aryl, etc.). A named R group will generally have the structure that is recognized in the art as corresponding to R groups having that name. For the purposes of illustration, representative R groups as enumerated above are defined herein. These definitions are intended to supplement and illustrate, not preclude, the definitions known to those of skill in the art.

The term "catalyst" is used herein to include all forms of catalysis, including classic initiators, co-initiators, co-catalysts, activating techniques, etc. For example, if an organometallic compound has a cationic charge, initiating a cationic polymerization in an ionic liquid, the organometallic will be referred to as a catalyst herein. Similarly, if the organometallic compound or complex operates in a coordination mechanism, it will still be referred to herein as a catalyst..

The term "hydrocarbyl" is used herein to refer to a radical having only carbon and hydrogen atoms, including, e.g., alkyl and the like.

The term "alkyl" is used herein to refer to a branched or unbranched, saturated or unsaturated, monovalent hydrocarbon radical. When the alkyl group has from 1-6 carbon atoms, it is referred to as a "lower alkyl." Suitable alkyl radicals include, for example, methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), n-butyl, t-butyl, i-butyl (or 2-methylpropyl), etc. In particular embodiments, alkyls have between 1 and

200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

"Substituted alkyl" refers to alkyl as just described including one or more groups such as lower alkyl, aryl, acyl, halogen (i.e., alkylhalos, e.g., CF_3), hydroxy, amino, phosphido, alkoxy, alkylamino, acylamino, acyloxy, aryloxy, aryloxyalkyl, mercapto, both saturated and unsaturated cyclic hydrocarbons, heterocycles and the like. These groups may be attached to any carbon of the alkyl moiety.

The term "aryl" is used herein to refer to an aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in benzophenone. The aromatic ring(s) may include substituted or unsubstituted phenyl, naphthyl, biphenyl, diphenylmethyl and benzophenone among others. In particular embodiments, aryls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

"Substituted aryl" refers to aryl as just described including one or more groups such as alkyl, acyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, phosphido, alkoxy, alkylamino, acylamino, acyloxy, mercapto and both saturated and unsaturated cyclic hydrocarbons which are fused to the aromatic ring(s), linked covalently or linked to a common group such as a methylene or ethylene moiety. The linking group may also be a carbonyl such as in cyclohexyl phenyl ketone. Specific examples of substituted aryl groups include $-C_6F_5$ and $-C_6H_3(CF_3)_2$.

The term "acyl" is used to describe a substituted carbonyl substituent, --C(O)J, where J is alkyl or substituted alkyl, aryl or substituted aryl as defined herein.

The term "amino" is used herein to refer to the group –NJJ', where J and J' may independently be hydrogen, alkyl, substituted alkyl, aryl, substituted aryl or acyl.

The term "alkoxy" is used herein to refer to the --OJ group, where J is an alkyl, substituted lower alkyl, aryl, substituted aryl, wherein the alkyl, substituted alkyl, aryl, and substituted aryl groups are as described herein. Suitable alkoxy radicals include, for example, methoxy, ethoxy, phenoxy, substituted phenoxy, benzyloxy, phenethyloxy, t-butoxy, etc.

As used herein, the term "phosphino" refers to the group –PJJ', where J and J' may independently be hydrogen, alkyl, substituted alkyl, aryl, substituted aryl or acyl.

As used herein, the term "mercapto" defines moieties of the general structure

J—S—J' wherein J and J' are the same or different and are hydrogen, alkyl, aryl or unsubstituted or substituted heterocyclic as described herein.

The term "saturated cyclic hydrocarbon" denotes groups such as cyclopropyl, cyclobutyl, cyclopentyl, etc. and substituted analogues of these structures.

The term "unsaturated cyclic hydrocarbon" is used to describe a monovalent nonaromatic group with at least one double bond, such as cyclopentene, cyclohexene, etc. and substituted analogues thereof.

The term "heteroaryl" as used herein refers to aromatic rings in which one or more carbon atoms of the aromatic ring(s) are substituted by a heteroatom such as nitrogen, oxygen or sulfur. Heteroaryl refers to structures that may be a single aromatic ring, multiple aromatic ring(s), or one or more aromatic rings coupled to one or more nonaromatic ring(s). In structures having multiple rings, the rings can be fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in phenyl pyridyl ketone. As used herein, rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc. or benzo-fused analogues of these rings are defined by the term "heteroaryl."

"Heteroarylalkyl" defines a subset of "alkyl" wherein the heteroaryl group is attached through an alkyl group as defined herein. For example, if R^2 is a heteroarylalkyl, the alkyl portion will be bonded to the atom from which R^2 emanates and the heteroaryl portion will be a "substituent" on the alkyl.

"Substituted heteroaryl" refers to heteroaryl as just described wherein the heteroaryl nucleus is substituted with one or more groups such as alkyl, acyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc. Thus, substituted analogues of heteroaromatic rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc. or benzo-fused analogues of these rings are defined by the term "substituted heteroaryl."

"Substituted heteroarylalkyl" refers to a subset of "substituted alkyls" as described above in which an alkyl group, as defined herein, links the heteroaryl group to the bonding point on the ligand.

The term "heterocyclic" is used herein to describe a monovalent saturated or unsaturated nonaromatic group having a single ring or multiple condensed rings from 1-12 carbon atoms and from 1-4 heteroatoms selected from nitrogen, phosphorous

sulfur or oxygen within the ring. Such heterocycles are, for example, tetrahydrofuran, morpholine, piperidine, pyrrolidine, etc.

The term "substituted heterocyclic" as used herein describes a subset of "heterocyclics" wherein the heterocycle nucleus is substituted with one or more functional groups such as alkyl, acyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc.

The term "heterocyclicalkyl" defines a subset of "alkyls" wherein an alkyl group, as defined herein, links the heterocyclic group to the bonding point on the molecule.

The term "substituted heterocyclicalkyl" defines a subset of "heterocyclic alkyl" wherein the heterocyclic nucleus is substituted with one or more groups such as alkyl, acyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc.

The term "scavenger" is used herein to mean a compound that does not substantially interfere with the reaction, but reacts with impurities or undesired species that may be present in the system. A "scavenger" is intended to refer to a compound that increases catalyst activity presumably by reacting with impurities or undesired species.

Additionally, abbreviations used herein include: Ph = C_6H_5, Me = methyl, Et = ethyl, Pr^i = isopropyl, TMS = trimethylsilyl, Mes = 2,4,6-$Me_3C_6H_2$, Fc = ferrocene, Bu^t = tertiary butyl, DMAT = o-dimethylaminotoluene, DME = dimethoxyethane, and TFA = trifluroacetate.

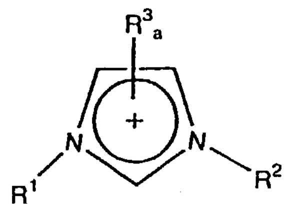
The term "polyisobutylenes" is used herein to refer to either homopolymers of isobutylene or copolymers of isobutylene and a suitable comonomer, which include acrylates, methacrylates, acrylonitriles, C_4-C_{20} butadienes, C_4-C_7 isoolefins, C_4-C_{12} diolefins, C_4-C_{12} conjugated diolefins, cationically polymerizable aromatics (such as indene and fulvenes) and styrene (each of which can be substituted or unsubstituted). More specific comonomers included within the definition of polyisobutylenes include those selected from the group consisting of piperylene, 2,3-dimethylbutadiene, 2,4-dimethyl-1,3-pentadiene, cyclopentadiene, methylcyclopentadiene, limonene, 1,3-cyclohexadiene, norbornadiene, isoprene, 1-butene, 2-butene, norbornene and combinations thereof.

The ionic liquids in the array(s) of this invention may be characterized by the general formula A^+B^- where A^+ is a cationic organic or inorganic molecule and B^- is an anionic organic or inorganic molecule. In some embodiments, A^+ can be linked to B^- forming a zwitterion. The mole fractions of A^+ and B^- in the ionic liquid may be varied to suit the reaction being studied. See for example, J. Chem. Tech. Biotechnol., 68, pp. 351-356 (1997), incorporated herein by reference. Mole fractions of A^+ and B^- in the ionic liquid are one variable that may be changed between members of the array of ionic liquids.

Many unsubstituted or substituted heterocyclic ring system may be converted into a stable cation A^+ through the process of alkyation or protonation or acylation or another method known to those of skill in the art. See for example T.L. Gilchrist "Heterocyclic Chemistry" (Wiley & Sons, 1995). Examples of unsubstituted or substituted heterocyclic ring systems that may converted into stable organic cations useful to this invention may be found in the Ring Systems Handbook (publication of the Chemical Abstracts Service 1993 Edition). These include (but are not limited to): imidazoles, pyrazoles, thiazoles, isothiazoles, azathiozoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiozoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophens, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophens, dibenzothiophens, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines, quinoxalines, quinolines, isoquinolines, thazines, oxazines, azaannulenes and the like.

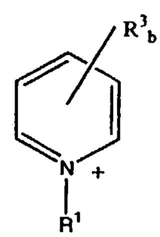
In addition, acyclic organic systems are also suitable and may be converted into stable organic cations A^+ in a similar manner. Examples include, but are not limited to amines (including amidines, imines, guanidines and the like), phosphines (including phosphinimines and the like), arsines, stibines, ethers, thioethers, selenoethers and the like.

In some embodiments, A^+ can be characterized by the general formula:



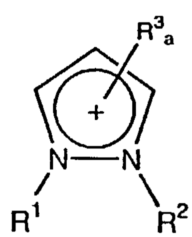
where R^1, R^2 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; and a is 0, 1, 2 or 3 signifying the number of R^3 groups attached to a carbon atom of the ring. In a preferred embodiment, R^1 is ethyl and R^2 is methyl.

In other embodiments, A^+ can be characterized by the general formula:



where R^1 and R^3 are as defined above and b is 0, 1, 2, 3, 4 or 5 signifying the number of R^3 groups attached to a carbon atom of the ring.

In other embodiments, A^+ can be characterized by the general formula:



where R^1, R^2, R^3 and a are as defined above.

In yet further embodiments, A^+ can be characterized by the either of the general formulas: $R^1R^2R^3R^4N^+$ or $R^1R^2R^3R^4P^+$ where each of R^1, R^2, R^3 and R^4 is

independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

In more specific embodiments, B^- may be represented by the general formula $AlR_{4-z}X_z^-$ where R is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; X is selected from the group of halogens (e.g., Cl, F, I and Br); and z is 0, 1, 2, 3 or 4. In other embodiments B^- may be selected from the group consisting of halogens, JX_4^-, PF_6^-, AsF_6^-, SbF_6^-, NO_2^-, NO_3^-, SO_4^{2-}, JR_4^- (where R is as defined above, X is as defined above and J is boron), substituted or unsubstituted carboranes , substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, substituted or unsubstituted carboxylates and triflates. B^- may also be a non-coordinating anion; see U.S. Patent 5,599,761, incorporated herein by reference. In many heterogeneous applications, B^- is an inorganic anion, such as $Al_2Cl_7^-$, Cl^-, JF_4^- (where J is boron), PF_6^-, $AlCl_4^-$ or a metal-organic anion.

In an alternative embodiment, an ionic liquid may comprise multiply charged cations or multiply charged anions, or both. For example:

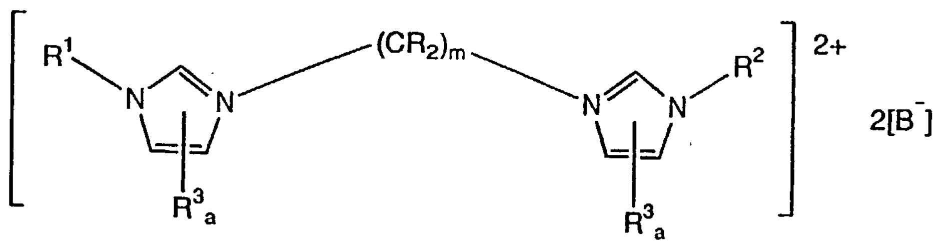
$A^{n+}\,B^{n-}$

$A^{n+}\,nB^-$

$nA^+\,B^{n-}$

where n is any positive integer greater than 1.

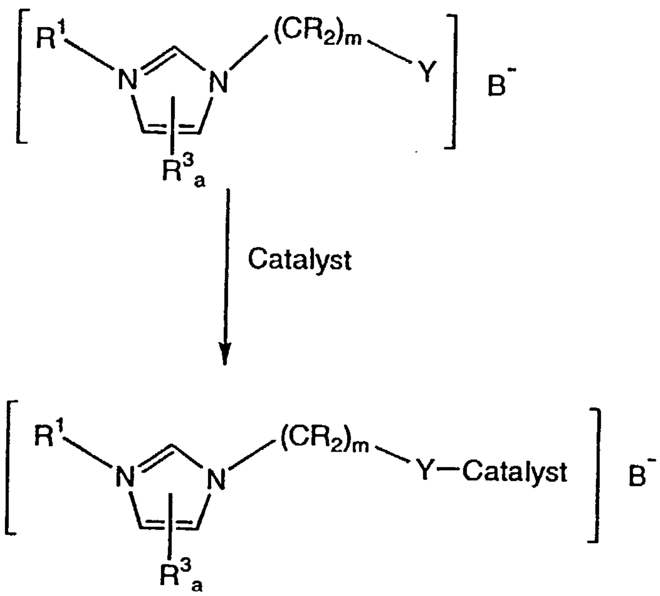
One example of an ionic liquid using a multiply charged ion is one that uses an imidazolium cation that may be represented by the following general formula:



where R, R^1, R^2, R^3 and a are as defined above, and m is an integer from 1-50. This example is depicted with an alkyl chain connecting the two-imidazolium moieties, but other connecting chains may also be used, such as substituted alkyls, substituted aryls and the like. Ionic liquids containing other multiply charged systems can also be used, including multiply charged cations prepared from the other unsubstituted or substituted heterocyclic ring systems or acyclic systems described above. Ionic liquids containing multiply charged ions may be mixed with ionic liquids containing singly charged ions to form useful catalyst combinations.

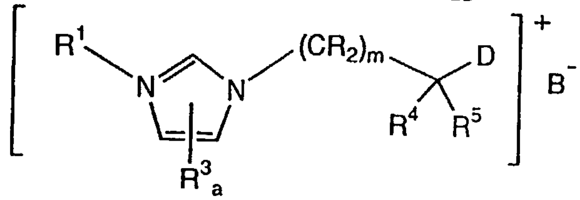
The ionic liquids used in this invention may be combined with reagents that may initiate cationic polymerizations, such as, but not limited to $JR_{3-y}X_y$, $AlR_{3-y}X_y$, alkylaluminoxanes, $GaR_{3-y}X_y$, $InR_{3-y}X_y$, $TiR_{4-z}X_z$, In(triflate)$_3$, $Ge[NR_2]_2$, $SnR_{4-z}X_z$, VCl_3, VCl_4, $VOCl_3$, $VOCl_2$, Sc(triflate)$_3$, $Yb[NR_2]_3$, $Ti(OPr^i)_4$, $CpTiMe_3$, Cp_2TiR_2, Cp_2ZrR_2, Cp_2HfR_2, $TiCl_3$, $ZrCl_3$, $HfCl_3$, $ZrCl_4$, $HfCl_4$, $Ti[(NR_2)_{4-z}R_z]$, $Zr[(NR_2)_{4-z}R_z]$, $Hf[(NR_2)_{4-z}R_z]$, $Zr[(NR_2)_{4-z}X_z]$, $Hf[(NR_2)_{4-z}X_z]$, $Ti[(NR_2)_{4-z}X_z]$, $La[NR_2]_2$, $Er[NR_2]_2$, $ThCl_4$, $ThOCl_2$, UCl_4, UCl_5, Cp_3U, $NbCl_5$, $TaCl_5$, $CrCl_2$, $Cr(TFA)_2$, $CrCl_3$, $Cr(TFA)_3$, $CrOCl_2$, CrO_2Cl_2, CrO_3, Cp_2Cr, $MoCl_3$, $MoCl_4$, $MoCl_5$, WCl_3, WCl_4, $FeCl_2$, $Fe(TFA)_2$, $FeCl_3$, $Fe(TFA)_3$, $Co(TFA)_2$, $Co(TFA)_3$, $Mn(TFA)_2$, $Ni(TFA)_2$, $Pd(TFA)_2$, $V(TFA)_3$, $V(TFA)_2$, Cu(TFA), Ag(TFA), SbX_5, PX_5, PX_3, POX_3, Cp_2AlR, HX, RX, water, alcohols, triflic acids, substituted or unsubstituted carboxylic acids, acylium ions, substituted alkyls, substituted aryls, $[Ph_3C][JR_4]$, $[R_3NH][JR_4]$, $[R_2OH][JR_4]$, $[Ph_3C][JX_4]$, $[Ph_3C][PF_6]$, $[Ph_3C][SbF_6]$, $[Ph_3C][AsF_6]$, $NaJR_4$, $LiJR_4$, KJR_4, $AgJX_4$, $AgJR_4$, $AgPF_6$, $AgSbF_6$, $AgAsF_6$, $AgNO_3$, $PbJX_4$, $PbJR_4$, $PbPF_6$, $PbSbF_6$, $PbAsF_6$, $PbNO_3$, $TlJR_4$, $TlPF_6$, $TlJX_4$, $TlSbF_6$, $TlAsF_6$, $TlNO_3$ and any combinations thereof. In the above list, R is defined as above; J is boron; y is a number 0, 1, 2 or 3; z is a number 0, 1, 2, 3 or 4; Cp is an unsubstituted or substituted cyclopentadienyl ring, substituted or unsubstituted indenyl, substituted or unsubstituted fluorenyl and the like such as bridging version of cyclopentadienyl, idenyl and fluorenyl complexes; X is a halogen, such as Cl, Br, I or F. Other initiators known to those skilled in the art may also be suitable.

In another alternative embodiment, the ionic liquid of this invention may contain a functional group, for example, that can act as a catalyst or scavenger. For example, the functional group may be attached directly to the cationic portion of the ionic liquid, such as is represented by the following general formula:



where R, R^1, R^3, a and m are as defined above, and Y is any functional group. In a preferred embodiment Y is capable of binding the catalyst or scavenger to a component of the ionic liquid. Alternatively, the catalyst or scavenger may be joined to the anion

(B^-) in a similar manner. In the example above an alkyl chain is used to tether the catalyst to the organic cation. Other tethers are known and may be used in this embodiment, such as those that are discussed in U.S. patent application no. 09/025,841, filed February 19, 1998, incorporated herein by reference. In this embodiment other stable ionic liquids can also be used, including ionic liquids containing multiply charged systems and ionic liquids comprising cations prepared from the other unsubstituted or substituted heterocyclic ring systems or acyclic systems described above. Additionally, functionalized ionic liquids from this embodiment may be combined with non-functionalized ionic liquids (containing singly or multiply charged ions) to form useful catalyst compositions. Ionic liquids from this embodiment may be combined with a catalyst or scavenger or any combination thereof to form a useful catalyst composition. An example of an ionic liquid of this embodiment is:



where R, R^1, R^3 a and m are as defined above; and R^4 and R^5 are defined as R^1 is defined above and D may be any halogen, SCN, CN, OH, OR, OCOR, COOR, O_2SR. This ionic liquid may be combined with a catalyst (and/or optionally a scavenger) such as those listed above to form useful catalyst compositions capable of preparing very high molecular weight polyisobutylenes.

The ionic liquids of this invention may be made by methods known to those of skill in the art. See for example, U.S. Patent No. 5,731,101 and WO 95/21871, both of which are incorporated herein by reference.

The ionic liquids of this invention can be catalysts alone, or may be combined with other compounds to form new catalytic compositions. Organometallic complexes may be added to the ionic liquids, with such complexes being any of those disclosed in commonly owned U.S. patent application no. 08/898,715, filed July 22, 1997, incorporated herein by reference. The catalysts useful with the ionic liquids are those that initiate a cationic polymerization reaction, including those listed above. See also WO 95/29940, incorporated herein by reference. Other mechanisms besides cationic polymerization may be at work in the presence of an organometallic complex, which may or may not have a charge. This specification is not limited to a cationic mechanism in conjunction with polymerization reactions.

The presence of the ionic liquid will have an effect on the polarity of polymerization mixture. Thus, depending on the type of process employed, the structure, yield, selectivity, molecular weight, etc. of the polymer product formed can vary. Since the ionic liquid can solubilize compounds that are ordinarily insoluble in organic solvents (e.g., metal complexes), the products can be readily separated from the ionic liquid, for example by decanting. Thus, this invention provides an easy method for removing product polymers from unwanted catalyst and avoiding additional ashing procedures for the removal of catalysts from polymer products. Therefore, this invention anticipates that novel polymers, copolymers or

interpolymers may be formed as a result of the processes of this invention, including polymers having unique physical and melt flow properties. Such polymers can be employed alone or with other polymers in a blend to form products that may be molded, cast, extruded or spun.

Polymerization can be carried out in a cationic process or in the Ziegler-Natta or Kaminsky-Sinn methodology, including temperatures of from -100°C to 400°C and pressures from atmospheric to 3000 atmospheres. Thus, the ionic liquids may serve only as the solvent for an organometallic compound or complex, which acts as the catalyst. There are numerous examples of catalytic organometallic complexes, such as mono-cyclopentadienyl or bis-cyclopentadienyl complexes. The organometallic compounds may be active catalysts or may be combined with an activator. When an activator or activating technique is used, those of skill in the art may use alumoxanes, strong Lewis acids, compatible noninterfering activators and combinations of the foregoing. See U.S. Patents 5,599,761, 5,616,664, 5,453,410, 5,153,157 and 5,064,802. Suspension, solution, slurry, gas phase or high-pressure polymerization processes may be employed with the catalysts and compounds of this invention. Such processes can be run in a batch, semi-batch or continuous mode. Examples of such processes are well known in the art. A support for the catalyst may be employed, which may be alumina, silica or a polymers support. Methods for the preparation of supported catalysts are known in the art. Slurry, suspension, solution and high-pressure processes use a suitable solvent as known to those skilled in the art.

In another embodiment, the ionic liquids of this invention form a portion of the reaction medium by mixing the ionic liquid with one or more co-solvents. Typically, this means that a two-phase solvent mixture is used for the reaction. Vigorous mixing is typically employed in this embodiment, but it is possible that proper selection of the ionic liquid and co-solvent(s) will mean that such mixing is not required. For example, the miscibility of the ionic liquid with the one or more co-solvents may result in a solvent system that does not appear to be a two phase solvent system. The miscibility of the ionic liquid with the co-solvent(s) can be adjusted by changing R, R^1, R^2 or R^3 in the above formulas for the ionic liquids to be more compatible with the co-solvent. For example if R is a long chain alkane, the ionic liquid will be more miscible with a hexane co-solvent. A long chain alkane is considered to be a C_{10}-C_{100} alkyl, for example. Co-solvents can be selected from the

group consisting of alkanes, substituted alkanes, aromatics and substituted aromatics. The use of a mixed solvent system (i.e., ionic liquid and co-solvent) may increase the solubility of certain organometallic complexes. See, Chauvin et al., *Ind. Eng. Chem. Res.*, Vol 34, No. 4, pp. 1149-1155 (1995).

Other Reactions useful to this invention include but are not limited to certain other organic transformations, such as cross-coupling reactions (e.g., Suzuki, Heck, aminations, Negishi, Meyers, Stille etc.), Friedel-Crafts, dimerization, oligomerization and polymerization reactions (e.g., Ziegler-Natta catalysts and other single-site coordination catalysts such as metallocenes may be used in the presence of an ionic liquids) as well as the other reactions listed herein.

For example, ionic liquids can be used to form two phases, leading to a large number of organic product mixtures useful in heterogeneous catalysis. In many cases this leads to a bi-phasic system which allows easy product separation and catalyst recycling. The lack of vapor pressure allows convenient removal of products through distillation. Of particular interest to catalysis are metal catalyzed reactions either by oxidized metals (e.g. Pd^{2+}) or by reduced metals (e.g. $Pd^{(0)}$). These metals could be in homogeneous solution or immobilized/heterogenized onto a support. Reduced metals can be unsupported (e.g., Pd black, nanoparticles, clusters, colloids) or supported (e.g., Pd/C). Metal ions can be reduced or activated in-situ in the ionic liquid (e.g., by contacting with a gaseous reducing agent). By proper choice (or high throughput screening of arrays of ionic liquids) of cations and anions the catalyst performance can be improved. For instance, the selection of anions ranges from basic, coordinating anions like Cl^- to acidic, non-coordinating anions like $Al_2Cl_7^-$ (as discussed above). The anions may have a significant role in the reactivity of the metal catalyst. In addition by adding co-solvents or modifiers the reactivity of the catalytic metal can be further enhanced. For example, transferring its coordinating Cl^- ligands to a Lewis acid can activate Pd ions. This process creates vacant sites in the coordination sphere of Pd ions for the interaction and activation of substrate species.

Thus, in general any catalyzed reactions using ionic liquids as at least part of the reaction media in a combinatorial format is part of this invention. Each of the candidate materials (*e.g.*, catalysts) being screened for a capability to enhance a chemical process of interest (*e.g.*, a chemical reaction) can be an element, a compound or a composition comprising a plurality of elements and/or compounds.

The candidate materials can be in a gaseous, liquid or solid phase. Solid-phase materials are preferred for some applications. The particular elements, compounds or compositions to be included in a library of candidate materials will depend upon the particulars of the chemical process being investigated. However, the particular chemical process being investigated is not critical, and can include chemical reactions and chemical separations, among others.

The chemical process is preferably a chemical reaction, which for purposes hereof, means a process in which at least one covalent bond of a molecule or compound is formed or broken. As such, immunoreactions in which immunoaffinity is based solely on hydrogen bonding or other forces – while chemical processes – are not considered to be chemical reactions. In general, the candidate materials of this invention catalyze reactions that include activation of, breaking and/or formation of H-Si, H-H, H-N, H-O, H-P, H-S, C-H, C-C, C=C, C≡C, C-halogen, C-N, C-O, C-S, C-P, C-B and C-Si bonds among others. Exemplary chemical reactions for which reaction-enhancing materials may be identified according to the present invention include, without limitation, hydrogenation, oxidation, dehydrogenation, aromatization, carbonylation, dehydrodimerization, hydrodehalogenation, hydrodesulfurization, oxychlorization, C-C coupling, Heck reaction, amination, amoxidation, alkylation, vinylation, acetoxylations, oxidative esterification, telomerization, hydroxylations of C=C bonds and aromatics, CH hydroxylation, oxidative cleavage, epoxidation, reduction, hydrogenation, dehydrogenation (including transfer hydrogenation), hydration, dehydration, hydrosilylation, hydrocyanation, hydroformylation (including reductive hydroformylation), carbonylation, hydrocarbonylation, amidocarbonylation, hydrocarboxylation, hydroesterification, hydroamination, hetero-cross-coupling reaction, isomerization (including carbon-carbon double bond isomerization), dimerization, trimerization, polymerization, co-oligomerization (e.g. CO/alkene, CO/alkyne), co-polymerization (e.g. CO/alkene, CO/alkyne), insertion reaction, aziridation, metathesis (including olefin metathesis), carbon-hydrogen activation, cross coupling, Friedel-Crafts acylation and alkylation, Diels-Alder reactions, C-C coupling, Heck reactions, arylations, Fries rearrangement, vinylation, acetoxylation, aldol-type condensations, aminations, reductive aminations, hydrodechlorinations, hydrodesulfurations and Fischer-Tropsch reactions, asymmetric versions of any of the aforementioned reactions, and combinations of any of the aforementioned reactions in

a complex reaction sequence of consecutive reactions. For chemical reactions, the candidate materials can be generally classified as those materials which are chemically altered or consumed during the course of the reaction (e.g., co-reactant materials, cataloreactants) and those materials which are not chemically altered or consumed during the course of the reaction (e.g., catalysts, selective blocking moieties). In preferred applications, the candidate materials are catalysts. As used herein, the term catalyst is intended to include a material that enhances the reaction rate of a chemical reaction of interest or that allows a chemical reaction of interest to proceed where such reaction would not substantially proceed in the absence of the catalyst.

The candidate materials preferably comprise elements or compounds selected from the group consisting of inorganic materials, metal-ligands and non-biological organic materials. In some applications, the candidate materials will consist essentially of inorganic materials, consist essentially of metal-ligand materials, or consist essentially of non-biological organic materials. Moreover, in some applications, the candidate materials will be compositions comprising mixtures of inorganic materials, metal-ligand materials, and/or non-biological organic materials in the various possible combinations.

Inorganic materials include elements (including carbon in its atomic or molecular forms), compounds that do not include covalent carbon-carbon bonds (but which could include carbon covalently bonded to other elements, e.g., CO_2), and compositions including elements and/or such compounds. Inorganic candidate materials that could be investigated according to the approaches described herein include, for example: noble metals such as Au, Ag, Pt, Ru, Rh, Pd, Ag, Os and Ir; transition metals such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Hf, Nb, Mo, Ta, W and Re; rare-earth metals such as La, Ce, Pr, Nd, Sm, Eu, Tb, Th, Dy and U; alloys of noble metals, transition metals and/or rare-earth metals; metal oxides such as CuO, NiO and Co_3O_4; noble-metal-doped metal oxides such as noble-metal-doped CuO, NiO and Co_3O_4; multi-metal oxides such as binary oxides of Cu-Cr, Cu-Mn, Cr-Mn, Ni-Cr, Ni-Mn, Ni-Cu, Ni-Mo, Cu-Mo, Ni-Co, Co-Mo, Ni-Fe, Fe-Mo, Cu-Fe, Mn-Ag, Mn-Sn, Ag-Sn, Cu-Ag, Cu-V, Ag-V, Cu-V, Ni-V, Bi-Mo, Bi-V, Mo-V, V-Zr, V-Ti, Zr-Ti, V-Nb, Nb-Mo, V-P, P-Mo, Ni-P, P-Cu, Co-P, Co-Fe, P-Fe, Mg-V, Mg-Sn, V-Sn, K-Ti, K-Bi, Ti-Bi, Cr-Sb, Cr-V, Sb-V, Bi-Mo, Bi-Nb, K-Cr, K-Al, Al-Cr, Zn-Cu,

Zn-Al, Cu-Al, La-Cr, La-Zr, Cr-Zr, La-Mo, Mo-Zr, La-W, W-Zr, Mo-W, W-V, Cu-W, Bi-W, Fe-Sb, Fe-V and Ni-Ta, Ni-Nb and Ta-Nb, and such as ternary oxides of Cu-Cr-Mn, Ni-Cr-Mn, Ni-Cu-Mo, Ni-Co-Mo, Ni-Fe-Mo, Cu-Fe-Mo, Mn-Ag-Sn, Cu-Ag-V, Cu-Ni-V, Bi-Mo-V, V-Zr-Ti, V-Nb-Mo, V-P-Mo, Ni-P-Cu, Co-P-Fe, Mg-V-Sn, K-Ti-Bi, Cr-Sb-V, Bi-Mo-Nb, K-Cr-Al, Zn-Cu-Al, La-Cr-Zr, La-Mo-Zr, La-W-Zr, Mo-W-V, Cu-Mo-W, Bi-Mo-W, Bi-V-W, Fe-Sb-V and Ni-Ta-Nb; metal carbides such as MoC, WC, PdC; metal sulfates, metal sulfides, metal nitrides, metal carbonates, metal chlorides, metal acetates, polyoxometallates (POM); metal phosphates such as vanadylpyrophosphates (VPO); Bronstead acids such as HF; Lewis Acids such as $AlCl_3$; and mixtures of any of the aforementioned inorganic materials, among others. Exemplary inorganic material libraries could include, for example, a triangular-shaped array of ternary metal oxides (e.g. such as oxides of the ternary metal partners described above) with single metal oxide compounds at each corners, binary metal oxide compositions along each of the sides with varying ratios of constituents, and ternary metal oxide compositions in the interior regions of the triangular array with varying ratios of constituents.

Quaternary rectangle-shaped arrays of metal oxides having 4 metals in each well and ternaries as the edges can be used. The inorganic materials do not have to be in the solid state to be catalytically active, although in many embodiments the materials will be in the solid state. Homogeneous solutions of atomically dispersed metal ions with inorganic, simple substituents (as opposed to complex ligands) and anionic counterions are one embodiment of the invention. The precursor can be a soluble solid salt of the metal or a stock solution. Examples are $Pd(OAc)_2$, $Pd(NO_3)_2$, $PdCl_2$, and $PdSO_4$. Redox active metals like the soluble salts of V, Cr, Mn, Fe, Co, Ni, Cu, Pd, Pt, Os, Rh, Re, Ru, Ce and Lewis acidic metals, like Al, B, Ga, Ge, Sn, Sb, Ir, Re, the rare earths, Ti, Zr, Zn, Fe, W, Mo are most common. Anions are simple and available like acetate, nitrate, sulfate, chloride, and oxalate. Libraries of inorganic candidate materials can be prepared, for example, according to the methods disclosed in U.S. Patent No. 5,776,359 to Schultz et al.

Metal-ligands comprise a central metal atom or ion surrounded by, associated with and/or bonded to other atoms, ions, molecules or compounds – collectively referred to as "ligands" – typically through a carbon (to form, e.g., an organometallic), nitrogen, phosphorous, sulfur or oxygen atom and/or one or more linker moieties. The

one or more ligands typically bind to one or more metal center and/or remain associated therewith, and by such association, modify the shape, electronic and/or chemical properties of the active metal center(s) of the metal-ligand complex. The ligands can be organic (*e.g.*, • ^{1}-aryl, alkenyl, alkynyl, cyclopentadienyl, CO, alkylidene, carbene) or inorganic (*e.g.*, Br^-, Cl^-, OH^-, NO^{2-}, *etc.*), and can be charged or neutral. The ligand can be an ancilliary ligand, which remains associated with the metal center(s) as an integral constituent of the catalyst or compound, or can be a leaving group ligand, which may be replaced with an ancillary ligand or an activator component. Exemplary metals / metal ions include ions derived from, for example, simple salts (*e.g.*, $AlCl_3$, $NiCl_2$, *etc.*), complex or mixed salts comprising both organic and inorganic ligands (*e.g.*, $[(\bullet\ 5\text{-}C_5Me_5)IrCl_2]_2$, *etc.*) and metal complexes (*e.g.*, $Gd(NTA)_2$, CuEDTA, *etc.*), and can generally include, for example, main group metal ions, transition metal ions, lanthanide ions, *etc.*

Libraries of metal-ligand candidate materials can be prepared, for example, according to the methods disclosed in PCT Patent Application WO 98/03521 of Weinberg et al. Briefly, a desired ligand can be combined with a metal atom, ion, compound or other metal precursor compound. In many applications, the ligands will be combined with such a metal compound or precursor and the product of such combination is not determined, if a product forms. For example, the ligand may be added to a reaction vessel at the same time as the metal or metal precursor compound along with the reactants. The metal precursor compounds may be characterized by the general formula $M(L)_n$ (also referred to as ML_n or $M\text{-}L_n$) where M is a metal and can include metals selected from the group consisting of Groups 5, 6, 7, 8, 9 and 10 of the Periodic Table of Elements. In some embodiments, M can be selected from the group consisting of Ni, Pd, Fe, Pt, Ru, Rh, Co and Ir. L is a ligand and can be selected from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, hydrido, thio, seleno, phosphino, amino, and combinations thereof, among others. When L is a charged ligand, L can be selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno,

and combinations thereof. When L is a neutral ligand, L can be selected from the group consisting of carbon monoxide, isocyanide, nitrous oxide, PA_3, NA_3, OA_2, SA_2, SeA_2, and combinations thereof, wherein each A is independently selected from a group consisting of alkyl, substituted alkyl, heteroalkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, and amino. Specific examples of suitable metal precursor compounds include $Pd(dba)_2$ (dba = dibenzylydieneacteone), $Pd_2(dba)_3$, $Pd(OAc)_2$ (Ac = acetate), $PdCl_2$, $Pd(TFA)_2$, (TFA = trifluoroacetate), $(CH_3CN)_2PdCl_2$, and the like. In this context, the ligand to metal precursor compound ratio is in the range of about 0.01:1 to about 100:1, more preferably in the range of about 0.5:1 to about 20:1. The metal atom, ion or metal precursor may be supported or not. Supports may be organic or inorganic. Similar to the ligands, the support may be an L. In other embodiments, the support will not form part of the metal precursor and suitable supports include silicas, aluminas, zeolites, polyethyleneglycols, polystyrenes, polyesters, polyamides, peptides and the like. Specific examples of Pd supported metals include Pd/C, Pd/SiO_2, $Pd/CaCO_3$, $Pd/BaCO_3$, Pd/aluminate, Pd/aluminum oxide, Pd/polystyrene, although any of the metals listed above could replace Pd in this list, e.g., Ni/C, etc. In other applications, the ligand will be mixed with a suitable metal precursor compound prior to or simultaneous with allowing the mixture to be contacted to the reactants. When the ligand is mixed with the metal precursor compound, a metal-ligand complex may be formed, which may be employed as a candidate material.

Non-biological organic materials include organic materials other than biological materials. Organic materials are considered to include compounds having covalent carbon-carbon bonds. Biological materials are considered to include nucleic acid polymers (e.g., DNA, RNA) amino acid polymers (e.g., enzymes) and small organic compounds (e.g., steroids, hormones) where the small organic compounds have biological activity, especially biological activity for humans or commercially significant animals such as pets and livestock, and where the small organic compounds are used primarily for therapeutic or diagnostic purposes. While biological materials are of immense commercial interest with respect to pharmaceutical and biotechnological applications, a large number of commercially significant applications involve chemical processes that are enhanced by other than

biological materials. Moreover, while fundamental screening approaches for many pharmaceutical and biological activities are known or readily adapted from known approaches, screening approaches for non-biological materials have not heretofore been widely investigated and reported. Although the candidate materials being screened are preferably not, themselves, biological organic materials, the candidate materials of the invention (e.g., inorganic materials) can be employed to enhance reactions directed to producing a biological organic material as the product of a chemical reaction (e.g., materials that enhance chemical-based, non-enyzmatic DNA synthesis, or materials that enhance a synthetic, non-enyzmatic route to a particular hormone or steroid).

In preferred applications, the candidate materials are catalysts being screened for catalytic activity and/or for catalytic selectivity for a chemical reaction of interest. The candidate catalysts can be homogeneous catalysts or heterogeneous catalysts. For homogeneous catalysis, the candidate materials are preferably solids or liquids which are soluble or miscible in the reaction medium under the reaction conditions, but can also include gasses. For heterogeneous catalysis, the candidate materials are preferably solids. In general, homogeneous candidate catalyst materials and heterogeneous candidate catalyst materials can include organic, inorganic and metal-ligand catalysts such as are described above.

Exemplary reactions for which a homogeneous catalyst may be investigated pursuant to the present invention, as well as known homogeneous catalysts for such reactions are shown in Table 1A. Exemplary reactions for which a heterogeneous catalyst may be investigated pursuant to the present invention, as well as known heterogeneous catalysts for such reactions are shown in Table 1B. The library of candidate catalysts being screened can be variations in the structure or composition of known catalysts or can be structurally unrelated thereto.

Table 1A: Exemplary Homogeneous Catalytic Reactions

Reaction Class	*Known Catalyst*
asymmetric C-C double bond isomerization	Ru-, Rh- ligand (e.g., phosphine)
Suzuki biaryl cross-coupling	Pd-ligand (e.g., phosphine)
hydroformylation	Co-, Rh- ligand (e.g., phosphine, phosphite)
hydrocarboxylation	Mo-, Pd-, Rh-, Co-, ligand (e.g., phosphine)
Heck reaction	Pd-ligand (e.g., phosphine)
hydrocyanation	Ni-ligand (e.g., phosphite)
assymetric hydrogenation	Ru-, Rh- ligand (e.g., phosphine)
Friedel-Crafts reaction	HF, $AlCl_3$
olefin polymerization	Zr-, Ti-, Hf- ligand (e.g. cyclopentadiene)
	Ni-, Pd- ligand (e.g., bis-imine)
olefin metathesis	Ru-, Mo- ligand (e.g., N-, P- based)
methanol carbonylation	Ir, Rh with halides (e.g., MeI, HI)
epoxide ring opening	Cu-ligand (e.g., alkoxide, amide, amine)
halogen exchange reaction (e.g., Ar-Br → Ar-F)	$R_4P^+X^-$ (X= halide)
hydrolysis (e.g., ethylene oxide → ethylene glycol)	H^+ source (e.g., H_2SO_4)
alcoholysis (e.g. ethylene oxide → glycol ethers)	Alkali hydroxide, Al_2O_3
ammonolysis (e.g., ethylene oxide → ethanolamines)	Heat
dimerization (e.g. ethylene oxide → 1,4-dioxane)	H^+ source
carboxylation	Mineral acids (e.g., H_2SO_4)
e.g., Koch-Haaf reaction	Lewis acids (e.g., BF_3, SbF_5)
electrophilic aromatic substitutions (e.g., nitration, sulfonation)	Mineral and Lewis Acids
esterification (direct, trans, poly)	Metal ions (e.g., Zn, Cu, Pb, Mn, Cd, Na, Li, Hg, Fe, Ni, Co, Ca)
halogenations (e.g. ethylene chlorination)	$FeCl_3$
isomerization (e.g., 1,4-dichlorobutene → 3,4-dichloro-1-butene)	PhCN,CuCl
oxidative carbonylation (e.g. Aniline → N-Phenethylurethane)	Pd + alkali iodide

Table 1B: Exemplary Heterogeneous Catalytic Reactions

Reactant(s)	*Product*	*Known Catalyst*
ethylene+acetic acid	vinyl acetate	Pd-Au
ethylene glycol	glyoxal	Cu
ethylene	ethyleneoxide	Ag
methanol	formaldehyde	Ag
butene dimerization	octene	Ni
HCl	Cl2	Cu-Fe-Cl, Cu-Cr-O
propylene	acrolein	Bi-Mo-O
acrolein	acrylic acid	Mo-V-O (+ Cu-Mo-O + W-O +Fe-Mo-O)
methacrolein	methacrylic acid	POM
o-xylene	Phthalic anhydride	V/TiO2
butane	maleic anhydride	VPO
toluene	benzonitrile	V-Sb-O, Fe-Sb-O, V_2O_5
ethylbenzene	styrene (non-ODH)	K-Fe-O
ethylbenzene	styrene (ODH)	K-Bi-O/TiO2
propane	propylene	K-Cr-O/Al2O3
vinyl cyclohexene	styrene	Cu/zeolite
cyclohexanol	cyclohexanone	Cu/SiO2
cyclohexene	benzene	NM/support
cyclohexylamine	aniline	NM/support
side chain aromatics	aromatic acids	Co-Mn-Zr-acetates (+Ce)
ethylene	acetaldehyde	Pd-Cu, Pd-Au
acetaldehyde	acetic acid	Mn-acetate
propylene	propylene oxide	Ti/silicalite
butadiene	vinyl oxirane	Ag
nitrobenzene	aniline	Cu/SiO2
beta-picoline	nicotinic acid	V-Mo/Ti-Zr-O
maleic anhydride	gamma-butyrolactone, tetrahydrofurane	Cu-Zn-O, Cu-Cr-O
propane	acrylic acid	V-Mo-Nb-O (+Te) (+Bi)
propane	acryl nitrile	(Fe, Ce, Cr, Co) BiMoO, MoTeFeSbO
benzene	phenol	Fe-Ga/zeolite
syngas	methanol	Cu-Zn/Al2O3
syngas	methane	Ni
syngas	fuel hydrocarbons	Fe, Co
H2+N2	ammonia	Fe
CH4+H2O	H2+CO	Ni
DeNOx		V/TiO2

The ionic liquids, catalysts, compositions and processes of this invention can be prepared and/or tested for in a combinatorial fashion. In this regard, the ionic

liquids, complexes or processes may be prepared and/or tested in rapid serial and/or parallel fashion, e.g., in a library or array format. When prepared in a library format, for example, the ionic liquids may take the form of one or more arrays comprising a plurality of compositions wherein each composition can be characterized by the general formula A^+B^- with the definitions above applying to this formula.

In a combinatorial array, each of the plurality of compositions (e.g., each ionic liquid) is somehow different from the other compositions in the array. Such differences can be compositional (such as composition of ionic liquid or ratio of ionic liquid to other reaction media or catalyst composition or metal complex to activator ratio or volume of solvent, etc.), processing parameters (such as temperature, pressure, atmosphere composition, etc.) or other differences that those of skill in the art will recognize from a review of this specification. Also typically, each composition in the array is at a selected region on a substrate such that each composition is isolated from the other compositions. This isolation can take many forms, typically depending on the substrate used. If a flat substrate is used, there may simply be sufficient space between regions so that there cannot be interdiffusion between compositions. As another example, the substrate can be a microtiter or similar plate having wells so that each composition is in a region separated from other compositions in other regions by a physical barrier.

The array typically comprises at least 10 different compositions, e.g., 10 different ionic liquids or 10 different mixed solvent systems including an ionic liquid or etc. In other embodiments, there are at least 25 compositions on or in the substrate each having a different chemical formula. In still other embodiments, there are at least 50 or 96 or 124 or more compositions on or in the substrate. Because of the manner of forming combinatorial arrays, it may be that each compound, material or composition is not pure. Typically, each compound, material or composition in the plurality is at least 50% pure within its region.

In still other embodiments, the library formed depends on how the desired reaction will be tested. For example, the libraries of this invention can be one or more arrays of ionic liquids, monomers and/or comonomers, solvents, catalysts, metal-ligand complexes or activators. Thus, if the portion of the reaction that is to be studied in parallel is the difference between ionic liquids, an array of ionic liquids having different compositions in the plurality can be formed and then used keeping all

other conditions of the reaction constant. Similarly, reaction conditions, processes, reactants, catalysts or solvents can be varied in a known manner using one or more arrays of the present invention.

Thus, this invention provides arrays of ionic liquids where each member of the array may be characterized by the general formula A^+B^- where A^+ represents any stable organic or inorganic cation and B^- represents any stable organic or inorganic anion. More specific definitions of A^+ and B^- are discussed above. The array can be formed in a plate that contain a plurality of vials, with each vial holding a member of the array of the ionic liquids, such that each member of the array cannot contact another member of the array. Alternatively the arrays can be in titer plate format, such as in a microtiter plate so that one member of the array cannot contact another member of the array.

One combinatorial research application is a method of discovering ionic liquids useful for particular reactions with the steps of the method comprising: providing an array of ionic liquids and running the reaction of interest in parallel using the ionic liquids in the array as a component in the reaction. The ionic liquid can be functioning in any of the capacities discussed above, such as the solvent, initiator, etc. Different ionic liquid compositions can be tested in the reaction of interest. Alternatively, each member of the array can contain the same ionic liquid allowing for process conditions of the reaction to be varied within the array. An example of this is shown in Example 1 where different members in the array contain the same ionic liquid, but are tested in a polymerization reaction carried out at different temperatures.

In more specific embodiments, ionic liquids for the polymerization of isoolefins or for the copolymerization of an isoolefin plus additional comonomer can be tested in a combinatorial manner. Here, an array of ionic liquids is provided with an aliquot of each member of the array being dispensed into a reactor block containing an array of reaction vessels. The reactor blocks discussed in the other incorporated patent applications and patents below can be used in this embodiment. The common theme among them is a plurality of reaction vessels for temperature or pressure controlled experiments. The other components of the polymerization reaction are added to the reactor vessels (e.g., monomer, initiators, co-initiators, co-solvents, etc.) and the reaction is carried out at desired reaction conditions, which may be

varied between two or more arrays or within a single array. The order of addition of reaction components depends on the reaction being studied. As discussed above, other compounds may be added to the ionic liquid to form a new catalyst composition, which polymerizes an isoolefin or copolymerizes the isoolefin plus additional comonomer. The preferred isoolefins are isobutylenes for creating polyisobutylenes.

The catalytic performance (activity and/or selectivity) of the compositions of this invention can be tested in a combinatorial or high throughput fashion. For any of the listed transformations, thin layer chromatography (TLC) in combination with imaging technology may be employed or accelerated liquid chromatographic techniques or accelerated characterization techniques may be used.. TLC is well known in the art, see for example Vol. 1, *Thin-Layer Chromatography, Reagents & Detection Methods,* Jork et al. (VCH Publishers, New York, New York 1990), incorporated herein by reference. For accelerated liquid chromatographic, gel permeation chromatography and other techniques, see provisional U.S. patent application no. 60/080,652, filed April 3, 1998, incorporated herein by reference. Polymerizations, oligomerizations and other reactions can also be performed in a combinatorial fashion, see, e.g., commonly owned U.S. Patent Application No. 09/177,170, filed October 22, 1998 (having Attorney Docket No. 65304-044), herein incorporated by reference. As shown in the examples of this specification, the reactions can be carried out under different reaction conditions, including temperature using a temperature controlled reactor block to hold the polymerization reactors. See commonly owned U.S. Patent Application No. 09/417,125, filed November 19, 1998 (having attorney docket no. 65304-014), incorporated herein by reference. High throughput screening can also be performed rapidly and/or optically and/or in parallel, for example, as disclosed in commonly owned U.S. Patent Applications 09/067,448, filed April 2, 1998, 08/947,085, filed October 8, 1997, 09/113,171, filed August 12, 1998, and 08/946,135, filed October 7, 1997, each of which is incorporated by reference.

EXAMPLES

When necessary, experiments were carried out in an inert atmosphere using nitrogen or argon as the inert gas and following practices standard to those of skilled in the art for these types of reactions (for example, see Shriver, D. F. The Manipulation of Air-Sensitive Compounds, 2nd ed. (New York : Wiley, c1986)). Except where noted, all starting compounds and solvents were obtained from J.T. Baker, Inc. or Aldrich and used without further purification. Dry solvents were obtained from Aldrich in Sure-Seal™ bottles and used without further purification. Deuterated solvents were purchased from Aldrich or Cambridge Isotopes, Inc. and used as is or dried according to standard procedures published in Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, 3rd Ed.*; Pergamon: New York, 1989.

The following polymerization examples were performed in a 96 well parallel reactor containing 96 individually stirred 1 ml glass vials. The reactor was a series of wells in a modular block that is described in U.S. Patent Application No. 09/417,125, filed November 19, 1998 (having attorney docket no. 65304-014). Thus, libraries of 96 polymerization reactions were examined in parallel.

Example 1/Library 1

In this example, an ionic liquid was used as a catalyst for the polymerization of isobutylene. The ionic liquid chosen for this library was 1-methyl-3-ethylimidazolium aluminum tetrachloride. The following 12 x 8 library was created by dispensing the following volumes of ionic liquid (Table 1) and isobutylene (Table 2) in microliters into the cryogenic reactor described above in the order presented (i.e., ionic liquid first and isobutylene last). Reaction temperatures were varied across the columns only (indicated by T = above columns 1-8, given in degrees centigrade).

Table 1: Ionic Liquid Volumes (μl)

row/column	1	2	3	4	5	6	7	8
	T = -65	T = -65	T = -40	T = -40	T = -30	T = -30	T = -20	T = -20
12	10	10	10	10	10	10	10	10
11	20	20	20	20	20	20	20	20
10	30	30	30	30	30	30	30	30
9	40	40	40	40	40	40	40	40
8	50	50	50	50	50	50	40	40
7	60	60	60	60	60	60	50	50
6	70	70	70	70	70	70	60	60
5	80	80	80	80	80	80	70	70
4	90	90	90	90	90	90	80	80
3	100	100	100	100	100	100	90	90
2	150	150	150	150	150	150	100	100
1	200	200	200	200	200	200	150	150
							200	200

The volumes of isobutylene dispensed into this library are shown below.

Table 2: Isobutylene Volumes (μl)

row/column	1	2	3	4	5	6	7	8
	T = -65	T = -65	T = -40	T = -40	T = -30	T = -30	T = -20	T = -20
12	483	483	483	483	483	483	483	483
11	461	461	461	461	461	461	461	461
10	439	439	439	439	439	439	439	439
9	418	418	418	418	418	418	418	418
8	396	396	396	396	396	396	396	396
7	374	374	374	374	374	374	374	374
6	352	352	352	352	352	352	352	352
5	330	330	330	330	330	330	330	330
4	308	308	308	308	308	308	308	308
3	286	286	286	286	286	286	286	286
2	400	400	400	400	400	400	400	400
1	400	400	400	400	400	400	400	400

The reaction temperature was set to –30 °C by setting the cryogenic reactor. After this setup, (i.e., following the addition of the isobutylene), the reaction was stirred for 1 hour whereupon the reaction was quenched with 30 microliters of ethanol. The reactor was opened up and the polymer from each library element was analyzed by rapid molecular weight gel permeation chromatography described in provisional U.S. patent application no. 60/080,652, filed April 3, 1998, incorporated herein by reference. The polymer yields and molecular weights are given below in Tables 3 and 4, respectively.

Table 3: Approximate Polymer Yields (given as percentages)

Row/column	1	2	3	4	5	6	7	8
	T = -65	T = -65	T = -40	T = -40	T = -30	T = -30	T = -20	T = -20
12	15	21	38	50	33	43	36	45
11	21	21	36	34	49	56	51	23
10	30	30	69	58	66	52	59	35
9	30	33	48	42	48	33	51	41
8	37	36	45	50	35	55	44	45
7	32	48	52	54	29	60	40	41
6	25	41	47	69	46	54	39	56
5	33	45	49	62	48	44	64	54
4	37	45	46	50	36	45	53	52
3	39	59	60	61	37	52	59	35
2	25	40	35	34	18	31	25	50
1	26	21	6	38	45	41	7	45

Table 4: Weight Average Molecular Weights

row/column	1	2	3	4	5	6	7	8
	T = -65	T = -65	T = -40	T = -40	T = -30	T = -30	T = -20	T = -20
12	66177	55468	526040	459950	302930	279870	116900	128060
11	60525	62186	503530	542320	304270	294820	120210	149450
10	930990	1032400	469940	517090	242660	289620	136570	141150
9	44152	46565	496040	511850	283400	304900	132130	158630
8	47410	44481	454700	512700	298200	302860	146610	146980
7	54803	48026	477890	503930	275940	241820	154920	160970
6	49543	48588	486100	509290	317170	302410	176400	153210
5	49771	43407	519060	461980	308430	312630	151980	141350
4	50672	44568	526990	487590	309750	297850	172690	163300
3	57416	42827	380190	466720	276400	280260	155010	148590
2	46973	44870	417900	259820	292350	247920	119080	72881
1	49798	47867	NA	405330	160910	146460	142250	80078

NA = Data Not available.

Example 2/Library 2

The following example represents the case where a catalyst was added to an ionic liquid to produce a new catalyst composition for the polymerization of isobutylene. The catalyst chosen for this library was ethylaluminumdichloride dispensed as a 1M solution in hexane. The polymerization was performed in hexane. The ionic liquid chosen for this library was 1-methyl-3-ethylimidazolium aluminum tetrachloride. The following 12 x 8 library was created by dispensing the following volumes of ionic liquid (Table 5), ethylaluminumdichloride (Table 6), hexane (Table 7) and isobutylene (Table 8) in microliters into the cryogenic reactor described above

in the order presented (i.e., ionic liquid first, ethylaluminumdichloride second, hexane third and isobutylene last).

Table 5: Ionic Liquid Volumes (μl)

row/column	1	2	3	4	5	6	7	8
12	10	10	10	10	10	10	10	10
11	20	20	20	20	20	20	20	20
10	30	30	30	30	30	30	30	30
9	40	40	40	40	40	40	40	40
8	50	50	50	50	50	50	50	50
7	60	60	60	60	60	60	60	60
6	70	70	70	70	70	70	70	70
5	80	80	80	80	80	80	80	80
4	90	90	90	90	90	90	90	90
3	100	100	100	100	100	100	100	100
2	50	50	50	50	100	100	100	100
1	0	0	0	0	0	0	0	0

Table 6: Volume of Ethylaluminumdichloride (μl of 1M solution in hexane)

row/column	1	2	3	4	5	6	7	8
12	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0
10	11	23	34	46	11	23	34	46
9	11	23	34	46	11	23	34	46
8	11	23	34	46	11	23	34	46
7	11	23	34	46	11	23	34	46
6	11	23	34	46	11	23	34	46
5	11	23	34	46	11	23	34	46
4	11	23	34	46	11	23	34	46
3	11	23	34	46	11	23	34	46
2	11	23	34	46	11	23	34	46
1	11	23	34	46	11	23	34	46

Table 7: Volume of Hexane (µl)

row/column	1	2	3	4	5	6	7	8
12	372	372	372	372	350	350	350	350
11	362	362	362	362	340	340	340	340
10	341	330	318	307	318	307	296	284
9	331	320	308	297	308	297	286	274
8	321	310	298	287	298	287	276	264
7	311	300	288	277	288	277	266	254
6	301	290	278	267	278	267	256	244
5	291	280	268	257	268	257	246	234
4	281	270	258	247	258	247	236	224
3	271	260	248	237	248	237	226	214
2	321	310	298	287	248	237	226	214
1	371	360	348	337	348	337	326	314

Table 8: Volume of Isobutylene (µl)

row/column	1	2	3	4	5	6	7	8
12	25	25	25	25	51	51	51	51
11	25	25	25	25	51	51	51	51
10	25	25	25	25	51	51	51	51
9	25	25	25	25	51	51	51	51
8	25	25	25	25	51	51	51	51
7	25	25	25	25	51	51	51	51
6	25	25	25	25	51	51	51	51
5	25	25	25	25	51	51	51	51
4	25	25	25	25	51	51	51	51
3	25	25	25	25	51	51	51	51
2	25	25	25	25	51	51	51	51
1	25	25	25	25	51	51	51	51

The reaction temperature was set to –30 °C by setting the cryogenic reactor. After this setup, (i.e., following the addition of the isobutylene), the reaction was stirred for 1 hour whereupon the reaction was quenched with 30 microliters of ethanol. The reactor was opened up and the polymer from each library element was analyzed as in Example 1. The polymer yields and molecular weights are given below in Tables 9 and 10, respectively.

Table 9: Approximate Polymer Yields (given as percentages)

Row/column	1	2	3	4	5	6	7	8
12	100	100	100	100	67	100	100	100

11	100	100	100	45	100	100	100	100
10	100	100	100	100	100	100	100	100
9	100	100	100	100	100	100	100	60
8	100	100	100	79	100	100	100	58
7	100	100	100	100	100	100	100	31
6	100	100	100	100	84	100	90	63
5	100	100	100	17	100	100	100	32
4	100	100	100	88	30	100	100	NA
3	NA	100	100	100	NA	100	100	NA
2	100	100	100	98	NA	100	100	NA
1	79	81	78	75	83	78	67	65

NA = Data Not Available

Table 10: Weight Average Molecular Weights

row/column	1	2	3	4	5	6	7	8
12	416250	384080	203760	515670	141300	110710	298250	217320
11	80309	66451	335600	421650	362990	299750	269390	220620
10	285220	61764	39044	51026	70941	39414	103730	109340
9	261320	222200	55577	73895	69419	46013	NA	142190
8	275590	235030	186310	250930	139960	145490	NA	191860
7	228140	188120	204440	228230	NA	123380	123350	176520
6	247290	211960	212890	250480	NA	135610	112070	163940
5	247860	201270	193620	202110	132010	121370	88619	162380
4	NA	230990	191740	202030	145570	118040	100270	139530
3	NA	209270	197170	167340	139230	147100	124360	108010
2	NA	224520	212170	193060	NA	147990	111690	149740
1	NA	196050	207050	205720	286190	112710	123920	132260

NA = Data Not Available

It is to be understood that the above description is intended to be illustrative and not restrictive. Many embodiments will be apparent to those of skill in the art upon reading the above description. The scope of the invention should, therefore, be determined not with reference to the above description, but should instead be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles and reference, including patent application and publication, are incorporated herein by reference for all purposes.

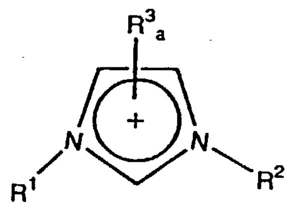
What is claimed is:

1. An array comprised of a plurality of members with each member comprising an ionic liquid characterized by the general formula $A^{+}B^{-}$ where A^{+} represents any stable inorganic or organic cation and B^{-} represents any stable organic or inorganic anion.

2. The array of claim 1 wherein A^{+} is a stable cationic molecule that is created by alkylation of a compound selected from the group consisting of imidazoles, pyrazoles, thiazoles, isothiazoles, azathiozoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiozoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophens, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophens, dibenzothiophens, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines.

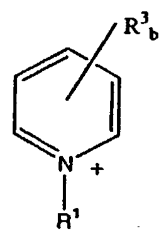
3. The array of claim 1 wherein A^{+} is a stable cationic molecule that is created by protonation or acylation of a compound selected from the group consisting of imidazoles, pyrazoles, thiazoles, isothiazoles, azathiozoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiozoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophens, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophens, dibenzothiophens, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines.

4. The array of claim 1 wherein A^+ can be characterized by the general formula:



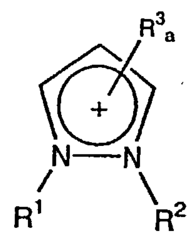
where R^1, R^2 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; and a is 0, 1, 2 or 3 signifying the number of R^3 groups attached to a carbon atom of the ring.

5. The array of claim 1 wherein A^+ can be characterized by the general formula:



where R^1 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; and b is 0, 1, 2, 3, 4 or 5 signifying the number of R^3 groups attached to a carbon atom of the ring.

6. The array of claim 1 wherein A^+ can be characterized by the general formula:



where R^1, R^2 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; and a is 0, 1, 2, or 3 signifying the number of R^3 groups attached to a carbon atom of the ring.

7. The array of claim 1 where A^+ can be characterized by the either of the general formulas: $R^1R^2R^3R^4N^+$ or $R^1R^2R^3R^4P^+$ where each of R^1, R^2, R^3 and R^4 is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

8. The array of claim 1 where A^+ is an acyclic organic compound capable of being converted into a stable organic cation, and the acyclic compound is selected from the group consisting of amines, phosphines, arsines, stibines, ethers, thioethers and selenoethers.

9. The array of claim 1 wherein B^- is represented by the general formula $AlR_{4-z}X_z$ where R is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl,

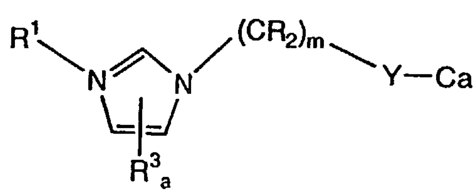
alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; X is selected from the group of halogens; and z is 0, 1, 2, 3 or 4.

10. The array of claim 1 wherein B^- may be selected from the group consisting of halide ions, JX_4^-, PF_6^-, AsF_6^-, SbF_6^-, NO_2^-, NO_3^-, SO_4^{2-}, JR_4^-, AlU_4^-, $Al_2U_7^-$, OAc^- substituted or unsubstituted carboranes , substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, borates, carbonates, substituted or unsubstituted carboxylates and triflates; and wherein J is boron and R is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

11. The array of claim 1, wherein each member of the array additionally comprises either a catalyst or an initiator.

12. The array of claim 1, wherein at least one member of the array of comprises a group that can act as a catalyst or scavenger and said group is covalently bonded to either A^+ or B^-.

13. The array of claim 13, wherein said group is attached directly to the cationic portion of the ionic liquid, so that A^+ may represented by the following general formula:

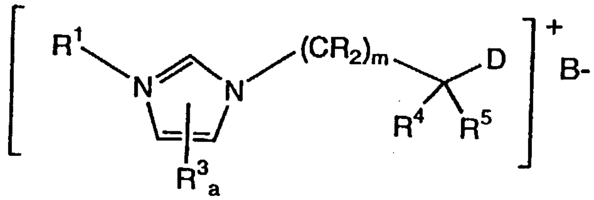


where each R, R^1 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R^3 groups

attached to a carbon atom of the ring; m is an integer from 1-50; Y is any functional group capable of binding the catalyst, initiator or scavenger; and Ca is the catalyst or scavenger.

14. The array of claim 13, wherein said group is covalently bonded to B^-.

15. The array of claim 1, wherein each member of the array may be characterized by the general formula:



where R, R^1, R^3, R^4 and R^5 are are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R^3 groups attached to a carbon atom of the ring; m is an integer from 1-50; and D is selected from the group consisting of halogen, SCN, CN, OH, OR, OCOR, COOR, O_2SR.

16. The array of claim 1, wherein there are at least 10 members in the array and said 10 members are different from each other.

17. The array of claim 17, wherein said difference is a difference in composition of the ionic liquid.

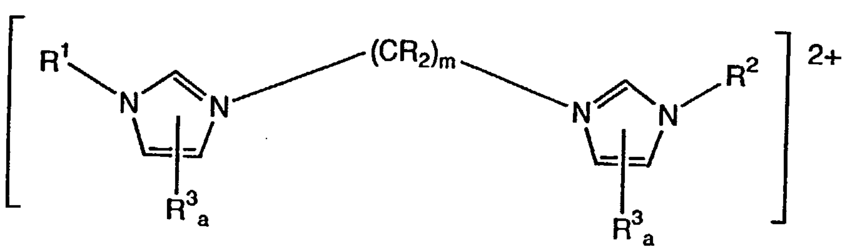
18. The array of claim 17, wherein said difference is a ratio of ionic liquid to other reaction media.

19. The array of claim 17, wherein said difference is selected from the group consisting of temperature, pressure, solvent and atmosphere.

20. The array of claim 17 wherein there are at least 25 members in the array that are different from each other.

21. An array comprised of a plurality of members with each member comprising an ionic liquid characterized by one of the general formulas $A^{n+} B^{n-}$, A^{n+} nB^- or nA^+ B^{n-} where n is any positive integer greater than 1 and where A^+ represents any stable inorganic or organic cation and B^- represents any stable organic or inorganic anion.

22. The array of claim 21, wherein A^+ may be represented by the following general formula:



where n is 2; R, R^1, R^2 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R^3 groups attached to a carbon atom of the ring; and m is an integer from 1-50.

23. The array of claim 22 wherein the CR_2 is replaced with a compound selected from the group consisting of substituted alkyls and substituted aryl.

24. The array of claim 21, wherein at least one member of said array additionally comprises a second ionic liquid characterized by the general formula A^+B^- where A^+ represents any stable inorganic or organic cation and B^- represents any stable organic or inorganic anion.

25. A process for the combinatorial testing an ionic liquid for suitability in a reaction, comprising:

mixing at least a portion of members of an array having a plurality of members, where each member comprises at least one ionic liquid characterized by the general formula A^+B^- where A^+ represents any stable inorganic or organic cation and B^- represents any stable organic or inorganic anion, with one or more potential catalysts in a parallel reactor having a plurality of reactor vessels corresponding to said plurality of said members; and

subjecting said plurality of reactor vessels to reaction conditions that cause a reaction in at least one of said plurality of reactor vessels.

26. The process of claim 26, wherein said reaction conditions are polymerization conditions comprising a temperature in the range of from –100°C to 300°C, at least one monomer that is an isobutylene and an inert atmosphere.

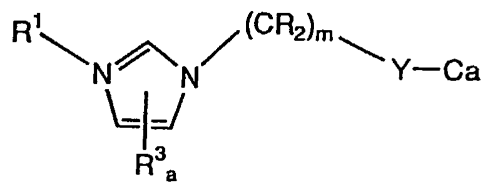
27. The process of claim 25, wherein said catalyst is an organometallic catalyst.

28. The process of claim 25 wherein A^+ is a stable cationic molecule selected from the group listed in any of claims 2, 3, 4, 5, 6, 7 or 8.

29. The process of claim 25 wherein B^- is selected from the group consisting those molecules listed in any of claims 9 or 10.

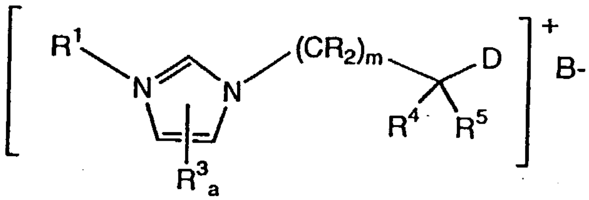
30. The process of claim 25 wherein at least one member of said plurality of ionic liquids contains a group that can act as a catalyst, initiator or scavenger and said group is covalently bonded to either A^+ or B^-.

31. The process of claim 30 wherein said group is attached directly to the cationic portion of the ionic liquid, so that A^+ may represented by the following general formula:



where each R, R^1 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R^3 groups attached to a carbon atom of the ring; m is an integer from 1-50; Y is any functional group capable of binding the catalyst, initiator or scavenger; and Ca is the catalyst, initiator or scavenger.

32. The process of claim 25 wherein at least one member of said array of ionic liquids may be characterized by the general formula:



where R, R^1, R^3, R^4 and R^5 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R^3 groups attached to a carbon atom of the ring; m is an integer from 1-50; and D is selected from the group consisting of halogen, SCN, CN, OH, OR, OCOR, COOR, O_2SR.

33. The process of claim 25, wherein at least one member of said array of ionic liquids is part of a two or more phase solvent system and another portion of said solvent system comprises a solvent selected from the group consisting of alkanes, cycloalkanes, Isopar E® and combinations thereof.

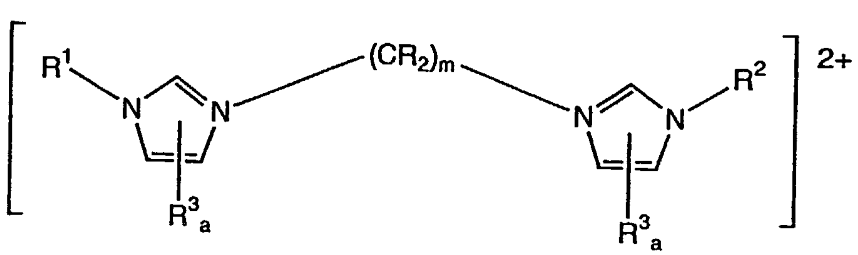
34. A process for combinatorial testing an ionic liquid for suitability in a reaction, comprising:

providing an array of ionic liquids having a plurality of members, where each member can be characterized by one of the general formulas $A^{n+}B^{n-}$, $A^{n+}nB^{-}$ or $nA^{+}B^{n-}$ where n is any positive integer greater than 1 and where A^{+} and A^{n+} represents any stable inorganic or organic cation and B^{n-} and B^{-} represents any stable organic or inorganic anion;

dispensing at least a portion of said plurality of members into a parallel reactor having a plurality of reactor vessels corresponding to said plurality of said members; and

subjecting said plurality of reactor vessels to reaction conditions that cause a reaction in at least one of said plurality of reactor vessels.

35. The process of claim 34, wherein A^{n+} may be represented by the following general formula:



where n is 2; R, R^1, R^2 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno,

and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R^3 groups attached to a carbon atom of the ring; and m is an integer from 1-50.

36. The process of claim 35, wherein the CR_2 is replaced with a compound selected from the group consisting of substituted alkyls and substituted aryl.

37. A process for combinatorial testing an ionic liquid for suitability in a reaction, comprising:

providing an array of ionic liquids having a plurality of members, where each member can be characterized by the general formula A^+B^- where A^+ represents any stable inorganic or organic cation and B^- represents any stable organic or inorganic anion;

dispensing at least a portion of said plurality of members into a parallel reactor having a plurality of reactor vessels corresponding to said plurality of said members;

subjecting said plurality of reactor vessels to conditions that cause a reaction in at least one of said plurality of reactor vessels; and

wherein said reaction is selected from the group consisting of cross-coupling, Friedel-Crafts, dimerization, oligomerization, polymerization, hydrogenation, oxidation, dehydrogenation, aromatization, carbonylation, dehydrodimerization, hydrodehalogenation, hydrodesulfurization, oxychlorization, C-C coupling, Heck reaction, amination, amoxidation, alkylation, vinylation, acetoxylations, oxidative esterification, telomerization, hydroxylations of C=C bonds and aromatics, CH hydroxylation, oxidative cleavage, epoxidation, reduction, hydrosilylation and hydroformylation.